STUDY OF STRUCTURAL AND BULK PROPERTIES OF $TiSi_2$ COMPOUND

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Physics, Indian Institute of Technology Hyderabad under the supervision of Dr. Manish K. Niranjan

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Signature of the Supervisor
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Certificate - I

The undersigned have examined the thesis entitled 'Study of Structural and Bulk Properties of $TiSi_2$ Compound' by **Maitraiyee Tiwai** is approved for the degree of Master of Science from IIT Hyderabad.

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CONTENTS

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CHAPTER 1

INTRODUCTION

In recent years, considerable efforts have been made to study the structural and microscopic properties of transition metal silicides. Silicides are compounds of silicon with more electropositive elements. Silicon is more electropositive than carbon. They are structurally closer to borides (a chemical compound between boron and a less electronegative element) than to carbides (a compound composed of carbon and a less electronegative element). Similar to borides and carbides, the composition of silicides cannot be easily specified as covalent molecules. The chemical bonds in them range from conductive metal-like structures to covalent or ionic.

Transition metal silicides are compounds of transition metals bonded to silicon. Transition-metal silicides are finding increasingly important applications in silicon integrated-circuit technology as schottky barriers, ohmic contacts, and low resistivity interconnects.

1.1 Schottky barrier: Whenever a metal and a semiconductor are in close contact, there exists a potential barrier between the two that prevents most charge carriers (electrons or holes) from passing from one to another. Only a small number of carriers have enough energy to get over the barrier and cross to the other material. When a bias is applied to the junction, it can have one of two effects: it can make the barrier appear lower from the semiconductor side, or it can make it appear higher. The bias does not change the barrier height from the metal side. The result of this is a schottky barrier (rectifying contact), where the junction conducts for one bias polarity, but not the other. Almost all metal-semiconductor junctions exhibit some of this rectifying behavior. Schottky diodes are used in many applications where other types of diode will not perform as well. They offer a number of advantages:

- Low turn on voltage**:** The turn on voltage for a diode is between 0.2 and 0.3 volts against 0.6 to 0.7 volts for a standard silicon diode. This makes it very much similar to a germanium diode.
- Fast recovery time**:** The fast recovery time because it has very small amount of stored charge and therefore it can be used for high speed switching applications.
- Low junction capacitance**:** In view of the very small active area, often as a result of using a wire point contact onto the silicon, the capacitance levels are very small.

Applications

The Schottky barrier diodes are widely used in the electronics industry finding many uses just like diode rectifier. Its unique properties have enabled it to be used in a number of applications where other diodes would not be able to provide the same level of performance. In particular it is used in areas including:

- RF mixer and detector diode: Schottky barriers can be used in radio frequency applications because of their high switching speed and high frequency capability. Therefore, they are used in many high performance diode ring mixers. In addition to this their low turns on voltage and high frequency capability and low capacitance make them ideal as RF detectors.
- Power rectifier**:** Schottky barrier diodes are also used in high power applications, as rectifiers. Their high current density and low forward voltage drop mean that less power is wasted than if ordinary PN junction diodes were used. This increase in efficiency means that less heat has to be dissipated, and smaller heat sinks may be able to be incorporated in the design.
- Power: Schottky diodes can be used in applications where a load is driven by two separate power supplies. One example may be a mains power supply and a battery supply. In these instances it is necessary that the power from one supply does not enter the other. This can be achieved using diodes. However it is important that any voltage drop across the diodes is minimized to ensure maximum efficiency. As in many other applications, this diode is ideal for this in view of its low forward voltage drop.
- Solar cell applications: Solar cells are typically connected to rechargeable batteries, often to lead acid batteries because power may be required for 24 hours a day and the sunlight is not always available. Solar cells do not like the reverse charge applied and therefore a diode is required in series with the solar cells. Any voltage drop will result in a reduction in efficiency and therefore a low voltage drop diode is needed. As in other applications, the low voltage drop of the Schottky diode is particularly useful, and as a result they are the favoured form of diode in this application.
- Clamp diode: Schottky barrier diodes are used as clamp diodes in a transistor circuit to speed the operation when it is used as a switch. They were used in this role in the 74LS (low power Schottky) and 74S (Schottky) sets of logic circuits. In these chips the diodes are inserted between the collector and base of the driver transistor to act as a clamp. To produce a low or logic "0" output the transistor is driven hard on and in this situation the base collector junction in the diode is forward biased. When the Schottky diode is present this takes most of the current and allows the turn off time of the transistor to be greatly reduced, thereby improving the speed of the circuit.

1.2 Ohmic Contact: It is a non-rectifying junction i.e. an electrical junction between two conductors that has a linear current–voltage (I-V) relationship as in Ohm's law. Low resistance ohmic contacts are used to allow charge to flow easily in both directions between the two conductors, without blocking due to rectification or excess power dissipation due to voltage thresholds.

Generally the term "ohmic contact" implicitly refers to an ohmic contact of a metal to a semiconductor, where achieving ohmic behavior is possible but requires careful technique. Metal–metal ohmic contacts are relatively simpler to make, by ensuring direct contact between

the metals without intervening layers of insulating contamination or oxidation, various techniques are used to create ohmic metal-metal junctions (soldering, welding, crimping, deposition, electroplating, etc.).

Applications:

Low-resistance, stable ohmic contacts to semiconductors are important for the performance and reliability of semiconductor devices, and their preparation and characterization are major efforts in circuit fabrication. Poorly prepared junctions of semiconductors can easily show rectifying behavior by causing depletion of the semiconductor near the junction, rendering the device useless by blocking the flow of charge between those devices and the external circuitry.

Ohmic contacts to semiconductors are typically constructed by depositing thin metal films of a particularly chosen composition followed by annealing to alter the semiconductor–metal bond.

Within this family of compounds, the refractory disilicides (i.e., those containing one of the groups IV-B, V-B, or VI-B elements) have attracted special attention because of their high temperature stability and their relatively low resistivity. Unlike the group VIII disilicides $CoSi_2$ and $NiSi_2$, which have the cubic fluorite structure, the refractory disilicides form with more complicated, low-symmetry orthorhombic (group IV-B), hexagonal (group V-B), and hexagonal-tetragonal (group VI-B) structures.

With advances in semiconductor device fabrication technology, the shrinkage in line width continues at a fast pace. The International Technology Roadmap for Semiconductors (ITRS) predicted that in 2005, in the 90 nm generation devices, the gate length and thickness of silicide at the contact window would be 32 nm and 20 nm, respectively. In the year 2007, for the 65 nm generation devices, these numbers are predicted to further decrease to 25 nm and 17 nm, respectively. In addition, more transistors will be incorporated in one chip. However, owing to the demand for increased integration level, the surface area will not be adequate to meet the interconnect demand. Multi-level interconnections provide flexibility in circuit design and a substantial reduction in die size and, thus, chip cost. Electrical connection between the various metal layers is provided by vertical interconnects commonly referred to as vias.

1.3 TITANIUM SILICIDE is one of the first few silicides considered for application in ultra-large scale integrated circuits (ULSI) owing to its low resistivity, good thermal stability and compatibility with Si processes. There are two ways of using titanium silicide in Si based devices: polycide gate electrode/interconnect in self- aligned silicide (SALICIDE) process. Because of the enormous potential of $TiSi_2$ in future technological applications, a comprehensive understanding of the bulk electronic properties for both the metastable (C49) and equilibrium (C54) phases is desirable.

With the help of software Quantum Espresso, I have performed various calculations such as the band structure, density of states, projected density of states, charge density and phonon calculations. Density Functional Theory (DFT) forms the basis of these calculations which is a sophisticated calculator which provides a tool to study multielectron systems. The bonding characters, electronic structure and how mechanical waves travel inside the crystal are described.

CHAPTER 2

CALCULATION METHOD

2.1 The tool which is used to study multielectron systems is Density Functional Theory. According to Quantum Mechanics, we can get all the information about a system if we are able to know about the wave function associated with it.

We would like to use SWE to compute the electronic structure of arbitrary atoms and molecules. By electronic structure, we mean the wave function for all the electrons in the system, for a fixed set of nuclear coordinates. Step 1 is to assume the nuclei to be fixed and then to solve the SWE (time independent) for all the electrons interacting with nuclei. Electronic structure provides the energies associated with the electron – electron and electron – proton interactions. Electrons can exist in any number of excited states, which correspond to eigenfunctions of the wavefunction , but typically we are interested in the one with lowest energy which is the ground state energy. Now, the complete wavefunction will have both electrons and protons in it but since mass of protons is too large when compared to the mass of electrons, electrons have faster degrees of freedom. So, we can write the total wavefunction as a product of nuclear and electronic wavefunctions. This is called the **Born- Oppenheimer Approximation**.

ψ_{tot}(nuclei, electrons) = ψ(nuclei)ψ(electrons)

The consequence of this approximation is that the total energy is now the sum of the nuclear energy and electronic energy. Nuclear energy is due to electrostatic repulsion of positively charged nuclei and electronic energy is due to electrons interacting with each other and with the nucleus.

$E_{tot} = E_{nuc}$ (nuclei- nuclei) + E_{elec}(electrons – nucleus + electrons – electrons)

Electronic structure calculations are basically done by mapping out the ground state energy surface i.e. the ground state electronic energy as a function of the positions of the nuclei.

So, it is easy to know about one body systems. They are as simple as solving the hydrogen atom problem which can be done analytically. The problem arises when there is more than one particle in a system. Multi particle systems are realistic systems where many electrons are moving in a potential generated by other electrons, atoms and external fields.

Problems with multielectron systems are:

- Electron orbitals can either have up or down spin. Each spatial orbital wavefunction can accommodate upto two spins.
- In distinguishability: Wavefunctions must change sign upon swapping the identities of two electrons.

Let us suppose that there is a multielectron system and so let the wave function associated with this system be $\psi(r_1, r_2,\ldots r_N)$ where $N = 10^{23}$. Here, it is more than just an accumulation of N electrons. The Schrodinger equation for such a system will be

$$\left[\frac{-\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}\sum_{I=1}^{M}\frac{Z_I e^2}{\left|\vec{r}_i - \vec{R}_I\right|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \frac{1}{2}\sum_{I=1}^{M}\sum_{J=1}^{M}\frac{Z_I Z_J e^2}{\left|\vec{R}_I - \vec{R}_J\right|}\right]\Psi(\vec{r}_1, \vec{r}_2, \ldots\ldots, \vec{r}_N$$

$$= E\Psi(\vec{r}_1, \vec{r}_2, \ldots\ldots, \vec{r}_N)$$

Solving this equation is near to impossible. So, what is it that we can do? We can see that the actual wave function of the system contains a lot of information about the system. While we are interested in the ground state energy and the charge density of the system, which are most important for practical purposes. We can know a lot about the system from the ground state energy and density distribution of the system. So, we are actually not interested in the complete wave function of the system.

Applying **Variational Theory**: Expectation value for the energy of any trial wavefunction will give an energy greator than or equal to the ground state energy of the true solution to SWE. Thus, we can find approximate solutions to SWE by minimizing the expectation energy with respect to a trial solution. We can pick an approximate form of the wave function for the polyatomic system. Then, find the optimal form of the function by minimizing the expectation energy with the true Hamiltonian with respect to any free parameters. Lower expectation energies mean better solutions.

Hartree- Fock Approach and Slater Determinant: The basic idea is to express the wavefunction as a product of individual spin orbital solutions which is known as the Hartree Product.

$\psi(1,2,3,\ldots.N) = \varphi_1(1)\,\varphi_2(2)\ldots.\varphi_N(N)$

$\varphi_1(1)\,\varphi_2(2)\ldots.\varphi_N(N) \neq -\,\varphi_1(2)\,\varphi_2(1)\ldots.\varphi_N(N)$

We use slater determinant here. We know that the wavefunctions of electrons are completely antisymmetric. By this statement we mean that under the exchange of any two particles' coordinates and spins the wavefunction changes sign. Inclusion of the spin degree of freedom complicates the matters a little bit, but the discussion is fairly simple for two electrons. When the total spin is conserved eigenfunctions of the Hamiltonian can also be chosen as the eigen functions of the total spin. If we consider the wave function of 1st electron which is at position 1 be $\varphi_1(1)$ and the 2nd electron at position 2 be $\varphi_2(2)$. So, the combined wave function which incorporates the exchange of electrons would be

$\psi(1,2) = (½)^{1/2} [\varphi_1(1)\, \varphi_2(2) - \varphi_1(2)\, \varphi_2(1)]$

For three or more particles, a general method is needed to construct electron wavefunctions which are completely antisymmetric in all cases. For this purpose, we can use the complete antisymmetry property of determinants. Since interchanging any two rows (or columns) of a determinant changes the sign of the determinant, completely antisymmetric wavefunctions can be expressed in the form of a determinant.

$$\Psi(1, 2, \ldots, N) = \begin{vmatrix} \phi1(1) & \phi1(2) & \ldots & \phi1(N) \\ \phi2(1) & \phi2(2) & \ldots & \phi2(N) \\ \ldots & \ldots & \ldots & \ldots \\ \phi N(1) & \phi N(2) & \ldots & \phi N(N) \end{vmatrix}$$

Putting in SWE:

$E = PE + KE + {}_{kl} - K_{kl})$

PE and KE are the potential and kinetic energies of the electrons in the field of nuclei. ${}_{kl}$ is the electrostatic repulsion between electrons and K_{kl} is the exchange interaction. It is due to the tendency of electrons with the same spin to avoid each other, per Pauli's exclusion principle.

The only difference between the 2 functions is that there is a swapping of identities in the 2nd set of orbitals. And finally the electron density is calculated.

2.2 **Density Functional Theory**: Complementary approach to Hartree – Fock theory for determining electronic structure is the DFT. Instead of computing the multielectron, multi-dimensional wavefunction, density functional theory is concerned with computing only the electron density.

Theorem by Hohenberg and Kohn: The ground state wavefunction and energy of a polyelectronic system is uniquely determined by a functional of the electron density.

The ground state energy functional is written as (given by Kohn and Sham)

$E[\rho(r)] = V(r)\, \rho(r)dr + E_{KE}[\rho(r)] + E_H[\rho(r)] + E_{XC}[\rho(r)]$

1st term: Interaction of electrons with external potentials

$V(r)\, \rho(r)dr = - \quad \rho(r)/(r-R_K)\, dr$

2nd term: Kinetic energy of the electrons (non- interacting)

3rd term: Hartree term: Electron- electron repulsive interactions

$E_H[\rho(r)] = ½ \quad [\, \rho(r_1)\, \rho(r_2)/(r_1 - r_2)]\, dr_1 dr_2$

4^{th} term: Exchange – correlation function. The exchange term can correspond to a quantum mechanical process by which particles are able to lower their energy. Correlation term contains everything else. Also, this term has the difference between the true kinetic energy value and the kinetic energy value obtained by considering non- interacting electrons. These terms are calculated by considering the system to be homogeneous. Some approximations like the local density approximation is used.

Local Density Approximation (LDA): The exchange–correlation (XC) energy functional in density functional theory (DFT) depends solely upon the value of the electronic density at each point in space. For regions of a material where the charge density is slowly varying, the exchange correlation energy at that point can be considered the same as that for a locally uniform electron gas of the same charge density.

$E_{XC}[(\rho(r)] = \rho(r)\, \epsilon_{XC}\, \rho(r)\, dr$

where, ϵ_{XC} is taken from simulations of homogeneous electron gas. This approximation, though simple is surprisingly accurate, and forms the core of most modern DFT codes. It even works reasonably well in systems where the charge density is rapidly varying. But it tends to predict lower atomic ground state energies and ionisation energies, while overpredicting binding energies. For these reasons there have been attempts to move beyond the LDA, notably through the addition of gradient corrections to incorporate longer range gradient effects (derivatives of density).

Generalized Gradient Approximation (GGA): As the LDA approximates the energy of the true density by the energy of a local constant density, it fails in situations where the density undergoes rapid changes such as in molecules. An improvement to this can be made by considering the gradient of the electron density in the energy functional.

$E_{XC} = E_{XC}\, [\rho(r),$

$\rho(r)]$

It is a large improvement over LDA results.

Density Functional Theory rests on 2 theorems proven by Kohn and Hohenberg, and the derivation of a set of equations by Kohn and Sham.
Theorem 1 says: Direct relation between the ground state wave function and the ground state electron density.
Theorem 2 says: The electron density that minimizes the energy of the above functional is the true electron density corresponding to the full solution to the SWE.
Self-consistent calculations are done to find the charge density.

The steps followed are:
Steps followed are as follows:

1. Define an initial, trial electron density.

2. Solve the Kohn-Sham equations using the trial electron density to find the single particle wave functions.

3. Calculate the electron density defined by the Kohn-Sham single particle wave functions from step 2.

4. Compare the calculated electron density with the electron density used to solve the Kohn-Sham equations. If they agree with some specified error, then compute the total energy from this density, otherwise update the trial electron density in some way.

5. Repeat.

The software we are using to perform various calculations to study the electronic structures is **Quantum ESPRESSO** which is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.
Quantum ESPRESSO stands for opEn Source Package for Research in Electronic Structure, Simulation and Optimization.

A **pseudopotential** or **effective potential** is used as an approximation for the simplified description of complex systems. To understand what a pseudopotential does, we note the following two facts about orbitals in condensed matter systems:

1. Lower energy orbitals can often be considered represent core electrons. These are electrons that are well localised around an atomic nucleus and whose properties do not change significantly with the atom's ``chemical environment''.
2. Orbitals representing electrons that are not core electrons oscillate very rapidly in the vicinity of atomic nuclei, but most of this oscillation can be put down to the fact that they have to be orthogonal to the core electrons.

A pseudopotential basically changes what the valence electrons “see”. The core electrons, and the potential due to effective nuclear charge, are replaced by a non-real potential that is defined such that the behaviour of the valence electrons is not affected outside of some cut-off radius from the nucleus. So long as this radius is not so large that it overlaps regions of space that are involved in chemical bonding, the pseudopotential approximation should not change the inter-atomic interactions that governs the behaviour of condensed matter.
Using pseudopotentials reduces the computational cost of a calculation in three ways:

1. By effectively removing core electrons from the calculation, the number of Kohn-Sham orbitals is reduced. This reduces the memory required to store the orbitals, the time required to evaluate orbital-dependent quantities, and the time required to orthonormalise a set of orbitals.
2. Because there are no core-electrons to which valence electrons must be orthogonal, there is less oscillation of the corresponding orbitals in the vicinity of the nucleus. This means that a lower cut-off energy can be used to represent the orbitals, resulting in lower

memory requirements and greater speed. This lowering of the cut-off energy is typically a few orders of magnitude resulting in massive gains in efficiency.

3. Because the pseudopotential is not uniquely defined for a particular element, we can optimise the shape of the potential so as to give as low required cut-off energy as possible. Again, this reduces memory and increases speed.

Now, we will look into the crystal structure of C49 $TiSi_2$ in the next chapter.

CHAPTER 3

CRYSTAL STRUCTURE

Crystal Structure is actually the space lattice plus the basis. **Space lattice** is an arrangement of infinite number of mathematical points in 3D space with each point having identical surroundings. **Basis** is an atom or a group of atoms at the lattice points which act as building units for the complete crystal structure.

$TiSi_2$ has two types of crystalline structures; one the base centered orthorhombic C49 structure and the other is face centered orthorhombic C54 structure.
Now, first I will introduce the concepts of symmetry operations and Bravais Lattices.

3.1 **Symmetry operations** transform the crystal to itself, i.e. a crystal remains invariant under a symmetry operation. There are four types of such operations:

1. Translations: Lattice point r, under lattice transformation vector operation T, gives another point r' which is exactly identical to r.

$$r' = r + T$$

2. Rotations: A lattice is said to possess the rotation symmetry if its rotation angle θ about an axis transforms the lattice to itself. Since the lattice always remains invariant by a rotation of 2π must be an integral multiple of θ i.e.

$$n\theta = 2\pi$$

$$\theta = 2\pi/n$$

   We have n= 1,2,3,4 and 6 fold rotation symmetry.

3. Reflections: A lattice is said to possess reflection symmetry if there exists a plane (or a line in 2D) in the lattice which divides it into 2 identical halves which are mirror images of each other. Such a plane (or line) is represented by m. Each allowed rotation axis can be associated with 2 possibilities: one is rotation with reflection and the other rotation without reflection. 5 rotation axes give rise to 10 allowed combinations.

4. Inversions: This operation is applicable to 3D lattices only. Each point located at r relative to a lattice point has an identical point located at –r relative to the same lattice point.

Rotation, Reflection and Inversion are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of space around a point. The group of such symmetry operations at a point is called a point group. In 2D, we have rotation and reflection combinations = 10. In 3D, inversion is added and the total combinations are = 32. Lattices consistent with point group operations are known as Bravais lattices.

Symmetry elements consist of combined point and translation operations. The group of all the symmetry elements of a crystal structure is called space group. It determines symmetry of a crystal structure as a whole. In 2D there are 17 distinct space groups and in 3D there are 230 distinct space groups.

Crystal systems which obey the point group symmetry are called Bravais lattices. In zero-dimensional and one-dimensional space, there is only one type of Bravais lattice. In two-dimensional space, there are five Bravais lattices: oblique, rectangular, centered rectangular (rhombic), hexagonal, and square.

In three-dimensional space, there are 14 Bravais lattices. These are obtained by combining one of the seven lattice systems (or axial systems) with one of the seven lattice types (or lattice centerings). In general, the lattice systems can be characterized by their shapes according to the relative lengths of the cell edges (a,b, c) and the angles between them (α, β, γ). The lattice types identify the locations of the lattice points in the unit cell as follows:

- Primitive (P): lattice points on the cell corners only (sometimes called simple)
- Body-Centered (I): lattice points on the cell corners with one additional point at the center of the cell
- Face-Centered (F): lattice points on the cell corners with one additional point at the center of each of the faces of the cell
- Base-Centered (A, B, or C): lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell
- Rhombohedral (R): lattice points on the cell corners only where $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$ (special case for the rhombohedral lattice system).

There are 7 lattice systems and 14 bravais lattices, namely: Triclinic, Monoclinic, Orthorhombic, Tetragonal, Rhombohedral, Hexagonal and Cubic.

Orthorhombic lattices result from stretching a cubic lattice along two of its orthogonal pairs by two different factors, resulting in a rectangular prism with a rectangular base (a by b) and height

(*c*), such that *a*, *b*, and *c* are distinct. All three bases intersect at 90° angles. The three lattice vectors remain mutually orthogonal.

C49 is base centered and C54 is face centered. C49 structure has 12 atoms per unit cell and is metastable while C54 has 24 atoms per unit cell and is stable. Unit cell is the smallest unit of the lattice, on continuous repetition, generates the complete lattice.

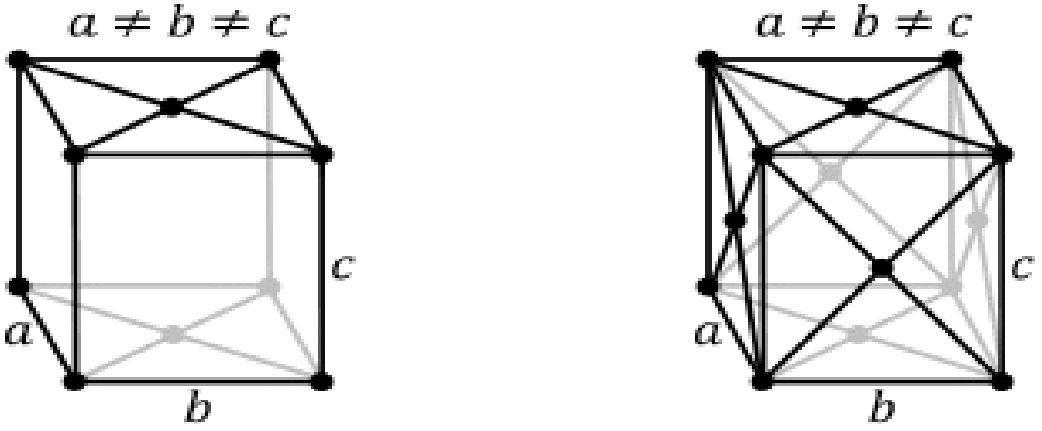


Figure 1: Base centered and Face centered orthorhombic crystals

3.2 Short Symbol: According to Herman – Mauguin Space Group symbol, symmetry elements contained in the short symbol are the minimum number needed to generate all of the remaining symmetry elements. The space group symbol is CmCm and the international number is 63. Here, first symbol is C which means centered; next 3 symbols denote symmetry in certain directions.

Schoenflies notation: C_n denotes rotation about some axis by an angle 360/n such that the system remains the same. S_n denotes rotation about an axis by an angle 360/n followed by a reflection through a plane perpendicular to the rotation axis. Hence the symbols are C49 and C54.

Structural data: Focus in this project is on C49 as there are lesser number of atoms per unit cell in this system. The Lattice parameters: a= 3.541 angs, b= 13.617 angs, c= 3.576 angs.

Composition	Structure	Spacegroup
$TiSi_2$	C49	Cmcm

Figure 2: Composition, structure and spacegroup of $TiSi_2$

The Unit cell looks like:

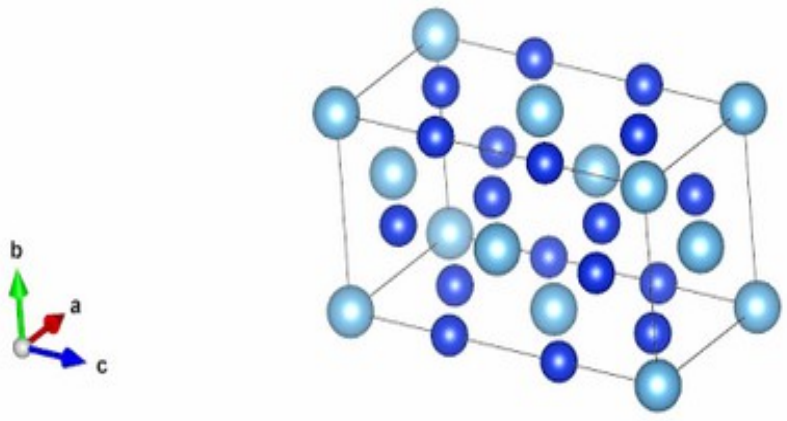


Figure 3: Unit Cell of $TiSi_2$

The big atoms are Titanium and the small atoms are Silicon.

CHAPTER 4

CALCULATIONS AND RESULTS

There are a few calculations which I have done in order to understand the electronic structure of C49 $TiSi_2$.

VC Relax calculations: Relaxation calculation is simply a series of self-consistent (scf) calculations with forces specified at each step and with updated positions after each iteration that corresponds to the strength of the forces between the atoms in the system. Here, atomic positions are first put in the input file which gets modified while the calculation takes place. The force strength between the atoms should not be more than 10^{-4} eV/angs.

There is also another way to relax the system by doing the relax calculations. In VC Relax calculations, electronic structure, shape, etc can be changed but while in Relax calculations, shape of the atom is fixed.

Lattice parameters (a = 6.69150)

1.0000	00000	00000
00000	3.8458	00000
00000	00000	1.0100
0.98068	000000	000000
000000	3.72747	000000
000000	000000	1.00034

Lattice parameters (a = 6.69151)

(a) (b)

Figure 4: (a) theoretical lattice parameters and (b) relaxed lattice parameters

The changes made in the lattice parameters and in the atomic positions came out to be less than 3%. This can be seen in figure1. Convergence was achieved in 16 iterations and total force acting is 0.000354.

Density of States Calculations: Density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied.
Unlike isolated systems, like atoms or molecules in gas phase, the density distributions are not discrete like a spectral density but continuous. A large DOS at a specific energy level means that there are many states available for occupation. A DOS of value zero means that no states can be occupied at that energy level. In general a DOS is an average over the space and time domains occupied by a system.

If we want to calculate the density of carriers in a semiconductor, we have to find the number of available states at each energy level. The number of electrons at each energy level is then

obtained by multiplying the number of states with the probability that a state is occupied by an electron. Since the number of energy levels is very large and dependent on the size of the semiconductor, we will calculate the number of states per unit energy and per unit volume.

Solving Schrodinger's wave equation gives us various energy states and corresponding wave functions associated with them. But when degeneracy comes into picture, the task of calculating each and every possible carrier wavefunction as well as its corresponding energy is impractical. Fortunately, rather than solving the SWE multiple times, we can find density of states. This is a function which when multiplied by an interval of energy, provides the total concentration of available states in that energy range.

Density of states function in 0D is $g(E) = 2\delta (E-E_c)$

Density of states function in 1D is $g(E) = 1/\pi h (m'/2(E-E_c)^{1/2}$

Density of states function in 2D is $g(E) = m'/h^2\pi$

Density of states function in 3D is $g(E) = 1/2\pi^2 (2m/h^2)^{3/2} \sqrt{E}$

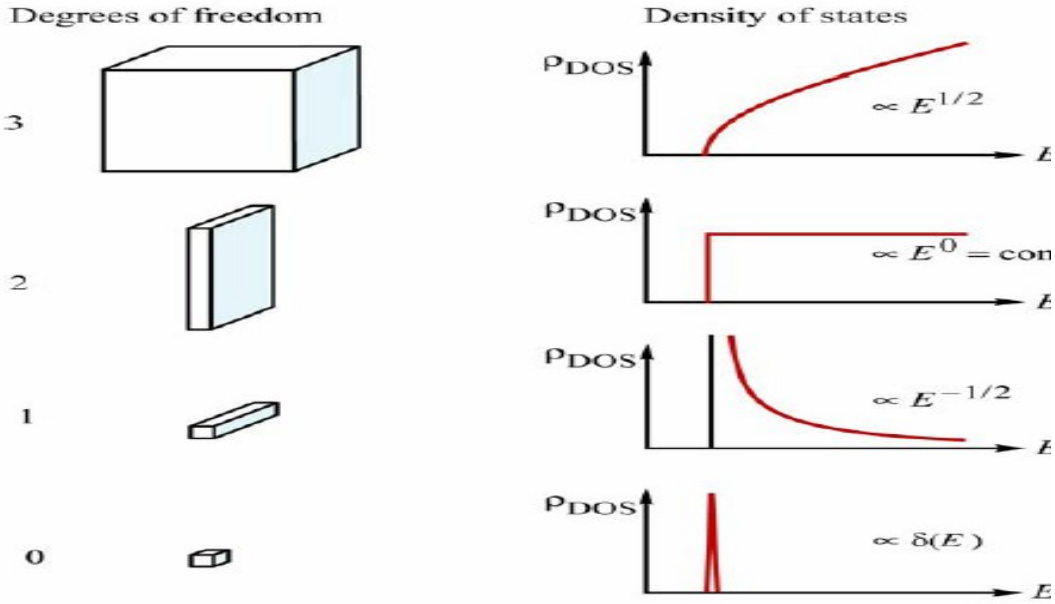


Figure 5: Density of States for 0D, 1D, 2D and 3D

Density of States:

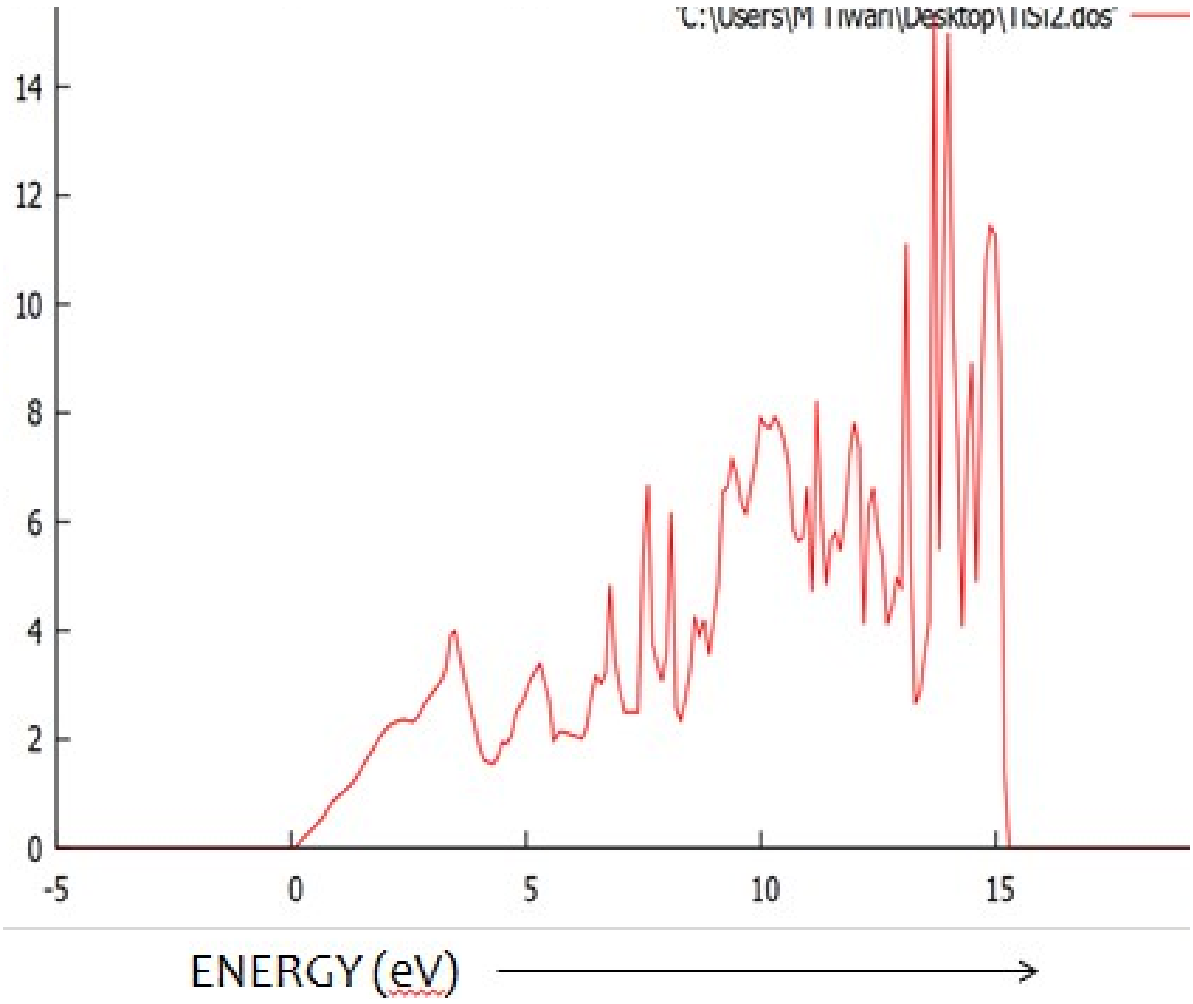


Figure 6: Density of states plot. The energy scale was taken from 0- 15 eV

My Fermi level is at 13.063eV. It is represented by the black line in the plot.

Inference

- The Fermi level lies in a dip of the DOS, which reduces the band-structure energy, and contributes to structural stability.
- A large number of available states just after the Fermi energy level suggest how good the thermal and electrical conductivities of the material are.
- A deep valley close to the Fermi energy E_f= 13.063eV, represents a pseudo gap (energy range with very few states associated with it) which indicates the presence of covalent bonding in $TiSi_2$.

- We can see that Fermi level falls below the pseudo gap, this indicates that there are some non-filled bonding states and some extra electrons are required to reach maximum stability in compound. This can be reason for the presence of an orthorhombic C49 metastable phase at low temperatures.

Results match appreciably well with the published literature.

Projected Density of States Calculations: If we want to know how much a particular orbital is contributing to the available energy states in a system then such calculations are carried out. It is actually calculating DOS for each orbital. From the results obtained it can be clearly seen that the d orbital of Ti contributes the most to the DOS. And this is exactly what we expect also, as the d orbitals are partially filled in the transition metals and can provide states for electrons to occupy. While, the s, p orbitals of Ti and Si are completely filled and will contribute very little to DOS. Also, the sum of all the individual density of states of each orbital will give the total DOS of the system which should coincide with the previous calculation result.

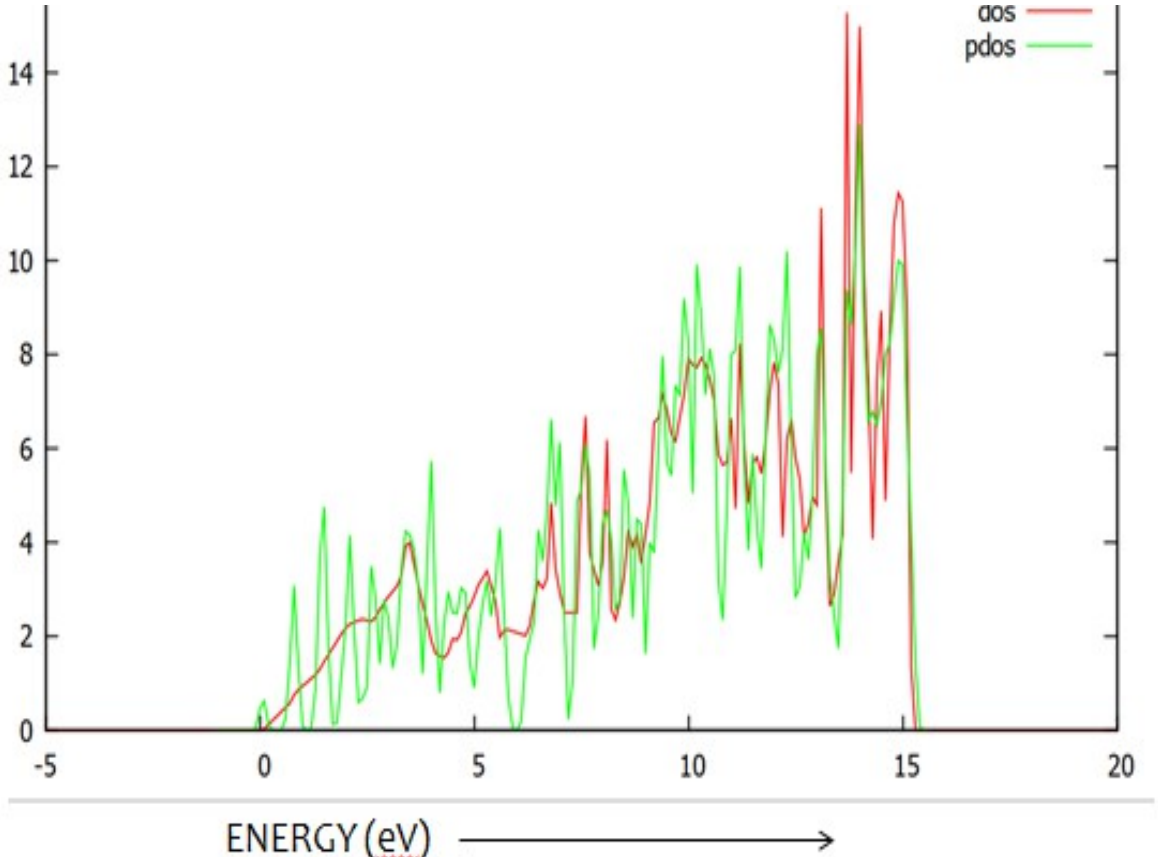


Figure 7: Projected density of states sum (green) i.e. contribution from all the orbitals are added up and then compared with the DOS (red).

The total projected density of states plot does not superimpose on the density of states plot but near the Fermi energy it comes close to the DOS plot. And this is what we expect, as the contribution due to the total wave functions should be similar to that of the DOS plot.

The d orbitals of Ti contribute the most to the total DOS. This is because the d – orbitals are partially filled in the relaxed state of the compound and can provide available states for electrons to occupy when the compound is excited and make it conducting in nature.

Here, we can compare by seeing the graph around the Fermi level. In the available literature, the Fermi level is shown by a dashed line. And the Fermi level in my calculations is at 13.063eV.

Band Structure Calculation: The electronic band structure of a solid describes those ranges of energy that an electron within the solid may have (called energy bands, allowed bands, or simply bands) and ranges of energy that it may not have (called band gaps or forbidden bands). Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid-state devices (transistors, solar cells, etc.).

The electrons of a single isolated atom occupy atomic orbitals. Each orbital is formed at a discrete energy level. When multiple atoms come together to form a molecule, their atomic orbitals combine to form molecular orbitals, each of which forms at a discrete energy level. As more atoms are brought together, the molecular orbitals extend larger and larger, and the energy levels of the molecule will become increasingly dense. Eventually, a collection of atoms forms a compound or a solid crystal. For this solid crystal, the energy levels are so close that they can be considered to form a continuum of levels for electrons to occupy. Hence, bands are formed.

Band gaps are some ranges of energy that are not covered by any band. This is due to finite widths of the energy bands. The bands have different widths which depend upon the degree of overlap in the atomic orbitals from which they arise. For example, the bands associated with core orbitals (such as 1s electrons) are extremely narrow due to the small overlap between adjacent atoms. Therefore, there are large band gaps between the core bands. Higher bands involve larger and larger orbitals with more overlap which then become wider and wider at high energy so that there are no band gaps at high energy.

The plot shows the values of $E_n(k)$ for values of k.

Band structure calculations are done exploiting the periodic nature of the crystal which leads to symmetry. For a single electron the Schrodinger wave equation give Bloch waves as solutions,

$$\psi_{nk}(r) = e^{i\,k.r} u_{nk}(r)$$

where, k is the wave vector . For every k, there are multiple solutions to the Schrodinger equation in terms of n, the band index, which simply numbers the energy bands. Each of these energy levels evolves smoothly with changes in **k**, forming a smooth band of states. For each band we can define a function $E_n(\mathbf{k})$, which is the dispersion relation for electrons in that band.

The wavevector can take any value inside the Brillouin zone, which is a polyhedron in wavevector space that is related to the crystal's lattice. Wavevectors outside the Brillouin zone

simply correspond to states that are physically identical to those states within the Brillouin zone. Special high symmetry points in the Brillouin zone are assigned labels like Γ, Δ, Λ, Σ.

It is usually difficult to visualize the shape of a band as a function of wavevector, as it would require a plot in four-dimensional space, E vs. k_x, k_y, k_z. Typically, band structure plots show values $E_n(k)$ in terms of k values along straight lines connecting symmetry points.

The high symmetry points taken are shown below. Any path taken through these points keeps the symmetry intact.

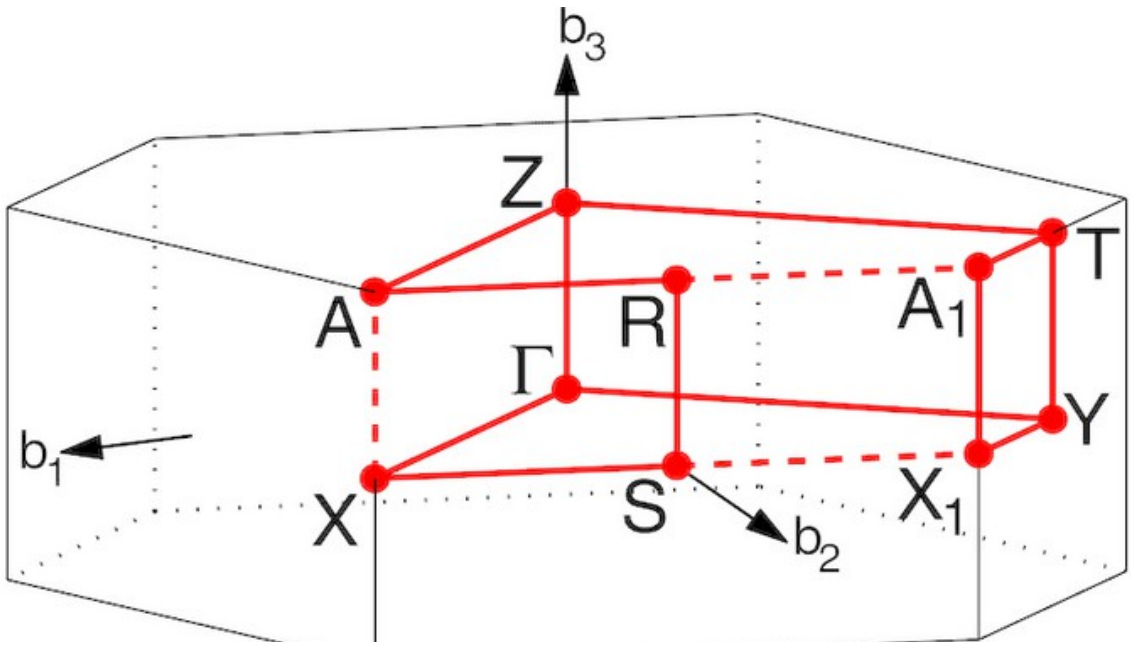


Figure 8: The high symmetry k points taking a path with which leaves the crystal invariant.

The plot for $TiSi_2$ shows that it is a conducting material. All bands near the Fermi energy overlap each other. No band gap is observed.

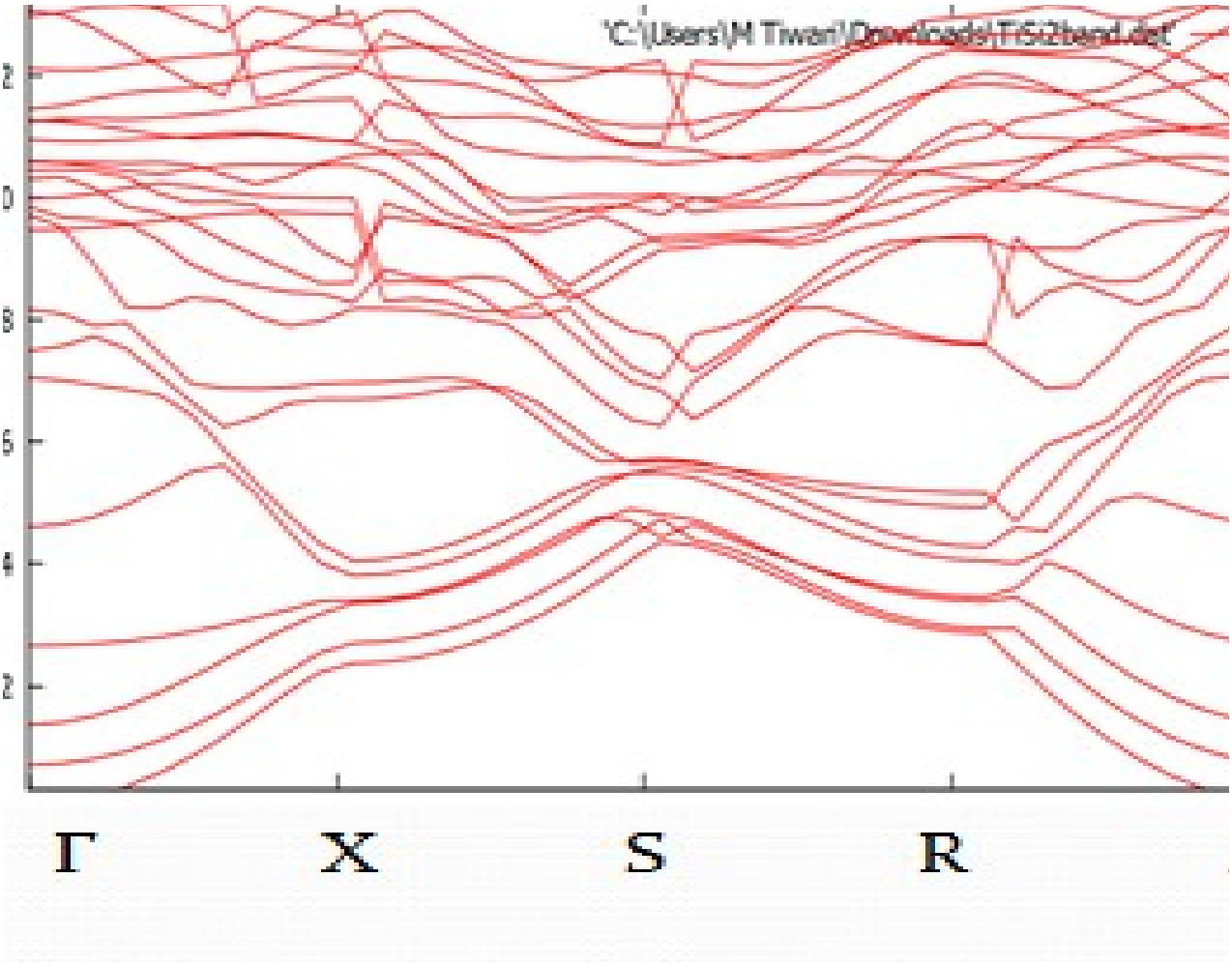


Figure 9: Band Structure plot of $TiSi_2$

Comparing with my result with a semiconductor's band structure (say Si)

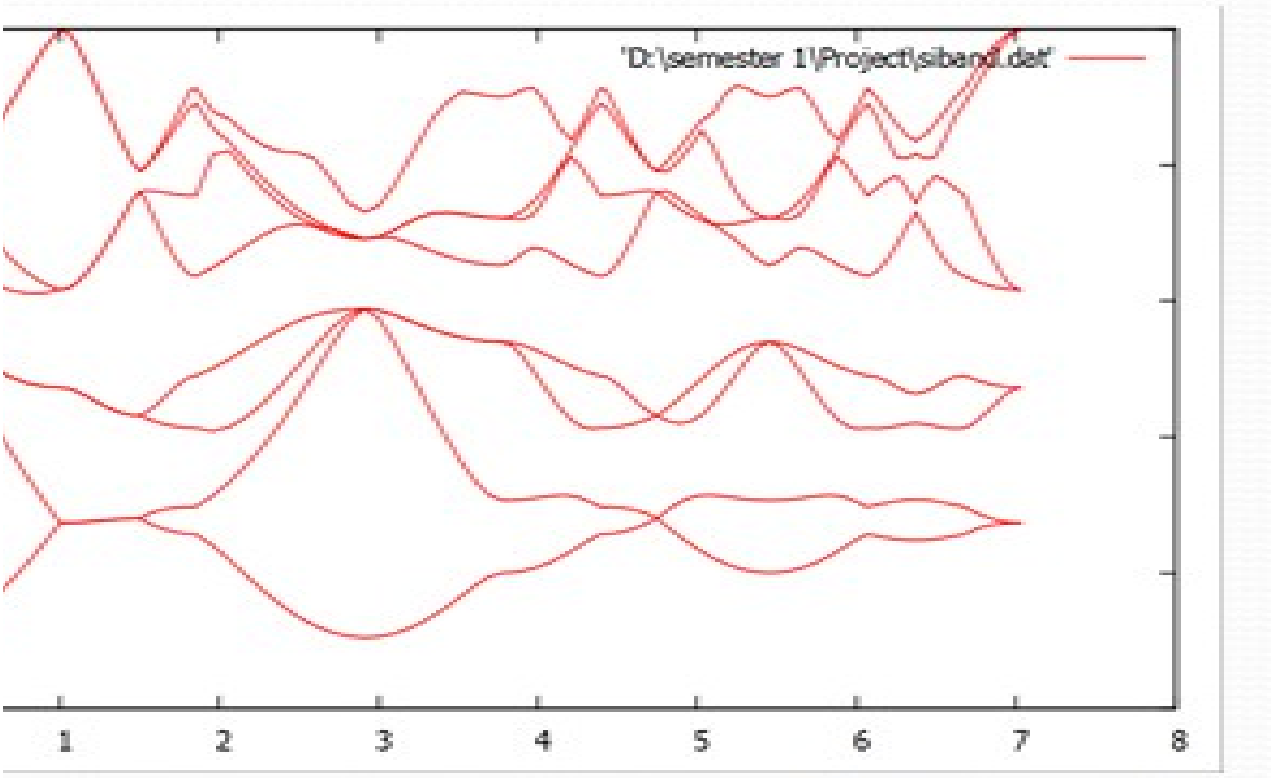


Figure 10: Band Structure plot of Si

Here, we can clearly see that there is a band gap in the Si's band structure which is exactly what we expect as it is a semiconductor but on the other hand $TiSi_2$ doesn't have any band gap. This suggests of it being a conductor.

Comparing $TiSi_2$ band structure with that of Ti, which is a metal.

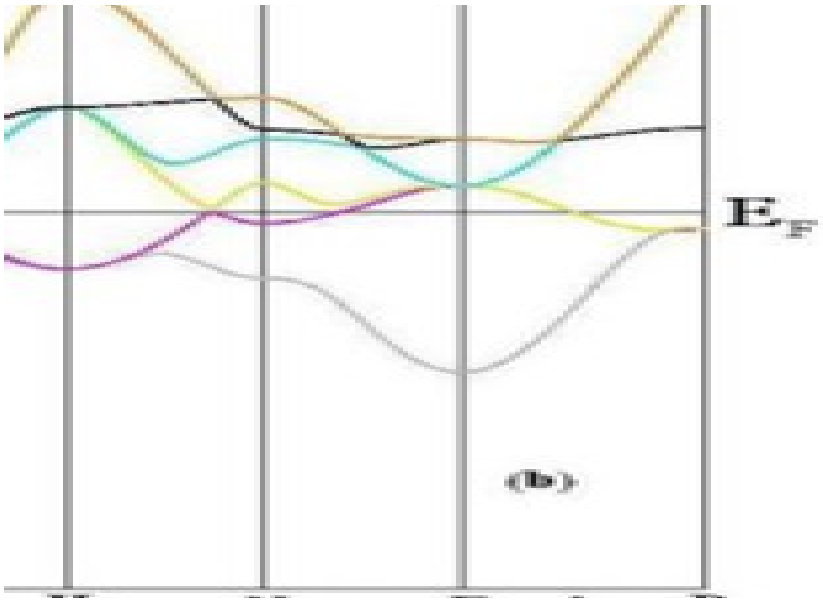


Figure 11: Band Structure plot of Ti

Inferences: Compound is overall conducting and exhibits metallic properties. Band structure is compared to that of Si (semiconductor) and Ti (metal) and it's clearly seen that $TiSi_2$ is more conducting than Ti as the band structure has more dispersion. This can be seen the orbitals are overlapping in the band structure. This compound has varied applications in areas where electrical conducting materials are required.

Charge Density Calculations: In order to understand the bonding properties of a solid, we need to look into the charge density inside the crystal. If we know how the charge is distributed within a crystal and what shape the charge clouds take around every atom inside the lattice, then we can know about the bonding in the crystal.

Atoms exert attractive and repulsive forces on each other.

Let us first look into the types of bonds that exist between atoms in various molecules and compounds.

1. Ionic Bonds: They are the strongest. These are formed when there is a transfer of valence electron from one atom which becomes a cation, to another atom which becomes an anion. The cohesive energy (energy released when 2 atoms are brought close to each other at an equilibrium distance r_0) is large is large in this case. eg: NaCl, etc.

2. Covalent Bonds: Their strength is lesser than that of ionic bonds. These are formed by sharing of valence electrons between 2 atoms. Orbitals of atoms overlap to form these bonds. They are directional in nature. This means the electrons are not shared equally, rather the more electronegative atom attracts the electrons towards itself more. eg: $MgCl_2$, etc.

3. Metallic Bonds: These bonds are weaker than covalent bonds. Electrons are free in this case i.e. electrons form like a sea around the ions in the solid. It is a delocalized sharing of electrons which is non-directional in nature. eg: in metals Cu, Ag, etc

The first 3 bonds are known as primary bonds.

4. Vander Waals Bonds: Strength is lesser than metallic bonds. Here, electrons remain associated with the original molecules. It is a dipole induced dipole interaction which is non- directional in nature. It exists in atoms or molecules which have their outermost shells completely filled and hence no tendency to gain, lose or share valence electrons with other atoms or molecules in the solid. eg: HCl, etc.

5. Hydrogen Bonds: These bonds are strong. When oppositely charged ends of permanently polarized molecules, each containing a hydrogen atom form a bond. eg: H_2O molecules

The last 2 bonds are known as secondary bonds.

With the help of software Xcrysden, I am able to get a charge density plot of C49 $TiSi_2$. XCrySDen is a crystalline and molecular structure visualisation program aiming at display of isosurfaces and contours, which can be superimposed on crystalline structures and interactively rotated and manipulated. It runs on GNU/Linux. Charge density contour plots of the C49 $TiSi_2$ are in the plane 010.

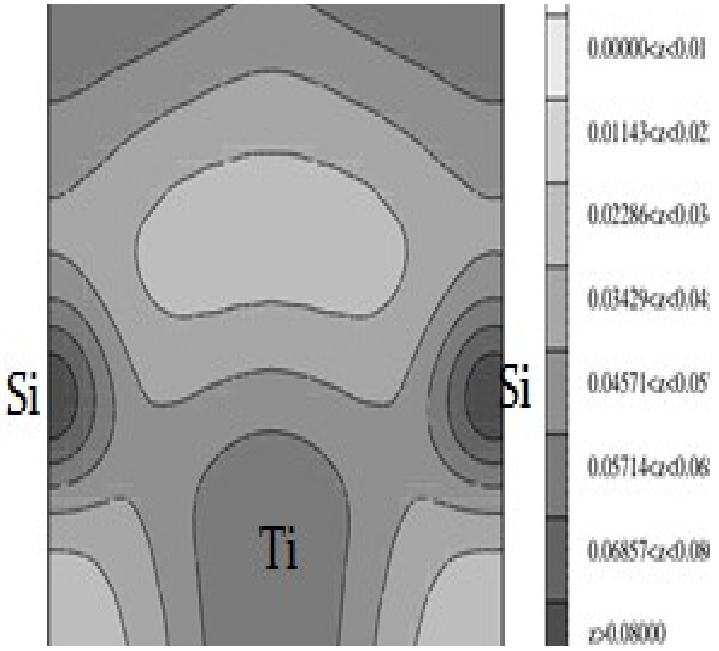


Figure 12: Charge density plot of $TiSi_2$

The curves in figure 8 represent the presence of a strong directional bonding between the Si atoms. Straight lines would have represented ionic binding. In this plane each face centered Ti atom is surrounded by six Si atoms. There is only a weak directional bonding between Ti and Si. The charge around the Ti sites is moved towards the Si atoms and this is what is expected of it due to the larger electronegativity of Si compared to Ti.

Comparing with the available literature data:

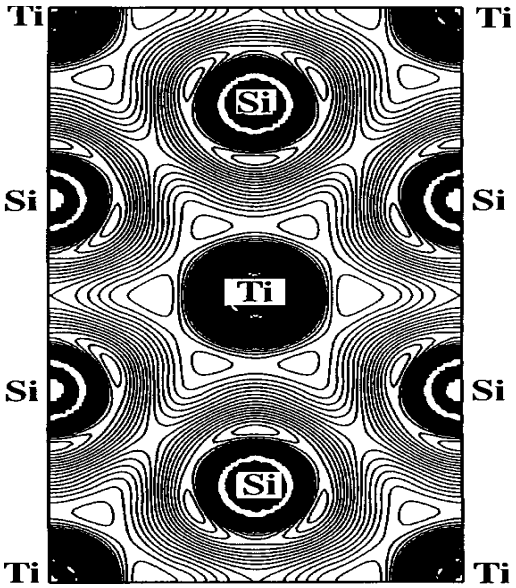


Figure 13: $TiSi_2$ charge density plot[1]

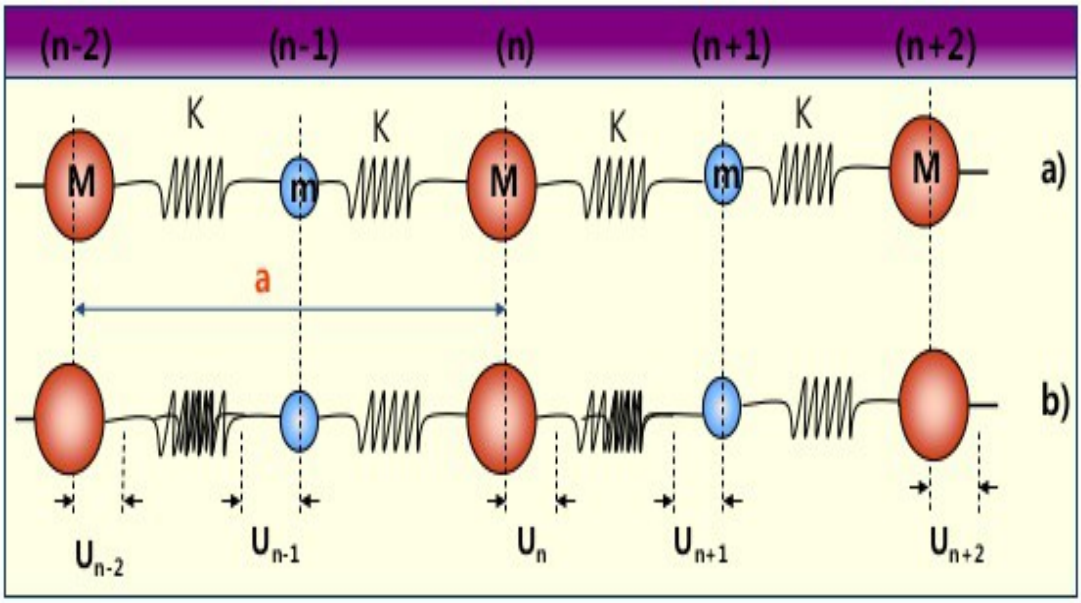
Inferences: Directional bonding in case of Si atoms. No directional bonding for Ti atoms. Very strong covalent and some metallic bonding is present in the compound.

Phonon Calculations: Let us begin with understanding lattice vibrations. A lattice may be considered as a regular arrangement of atoms which are joined together by elastic springs. If we take an example of a 2 dimensional lattice, the motion of any single atom affects all other atoms i.e. we have coupled motion of atoms. The lattice may vibrate freely in its normal modes due to its internal energy or may experience forced vibrations under the effect of external forces which may be mechanical or electromagnetic in nature. Normal modes give information about the thermal properties of solids, such as specific heat and thermal conductivity.

Now, let us look into the vibrations of 1D diatomic lattice.

Considering a 1D primitive lattice, with a basis set consisting of 2 atoms of masses m and M placed alternatively. The frequencies with which the lattice is vibrating are

$$\omega^2 = \frac{K(M+m)}{Mm} \pm K\sqrt{\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2(ka/2)}$$



Here, a is repeating distance, the nearest neighbors separations is a/2

Figure 14: Two different types of atoms M and m are connected by identical springs of spring constant K

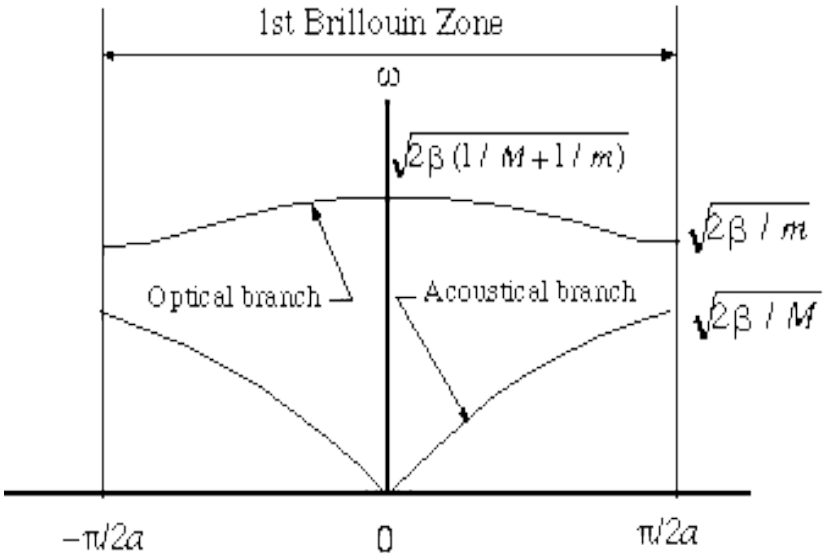


Figure 15: Dispersion relations for linear diatomic lattice showing acoustical and optical modes

When k tends to 0, it corresponds to the acoustic branch and when k tends to π/a, it corresponds to the optical branch.

- Acoustical branch resembles the dispersion relationship curve for a monoatomic lattice, whereas the optical branch represents an entirely different type of wave motion.
- Forbidden band: It is impossible to excite vibrations in a lattice at a frequency which lies inside this band. This means there is no travelling wave (when a wave is not confined to a given space along the medium) solution.
- Width of the forbidden band depends on the mass ratio M/m. Larger this ratio, greator the width. If M = m, the optical and acoustical branches coincide at k = π/2a and the forbidden gap disappears.
- 1st Brillouin zone lies in the region $-\pi/2a < k < \pi/2a$.

The vibrations of the acoustical branch can be excited by a force which makes the atoms in a crystal move in the same direction. This can be produced by directing a beam of sound waves on the surface of the crystal and hence the name acoustical vibrations.

The vibrations of the optical branch can be excited by a force which makes the neighbouring atoms move in opposite directions. Optical radiations can induce this type of vibrations in crystals and hence the name optical vibrations.

The only requirement to have such vibrations in a lattice is presence of 2 atoms per primitive cell.

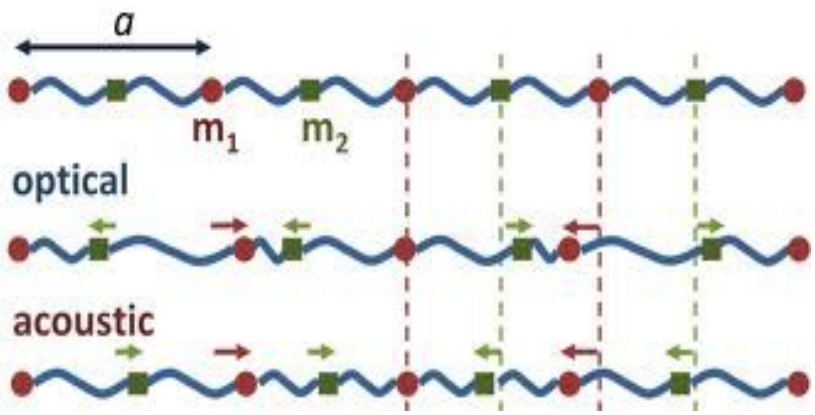


Figure 16: Optical and Acoustical vibrations in a crystal with 2 types of atoms

We know that quantum of energy of electromagnetic wave is a photon. Similarly, the energy of a lattice vibration or an elastic wave is also quantized and a quantum of this energy is known as phonon. All types of lattice vibrations in crystal comprise phonons – thermal vibrations are thermally excited phonons, sound waves are acoustical phonons and excitations of the optical branch generate optical phonons.

In C49 $TiSi_2$ there are 12 atoms per unit cell therefore 36 modes of vibrations. 3 correspond to the acoustical vibrations and the rest are optical vibrations. Every acoustical mode corresponds to a dimension in space. Hence, we have 3 acoustical modes.

Due to some numerical inaccuracies the interatomic force constants and the effective charges do not strictly satisfy some rules due to translational invariance of the system:

Translational rules $\sum_{\mathbf{L},j} C_{\alpha i,\beta j}(\mathbf{R}_\mathbf{L}) = 0 \qquad \forall\ \alpha, \beta \text{ and } i$

$\sum_{i} Z^*_{j,\alpha\beta} = 0 \qquad \forall\ \alpha, \beta$

Reasons for numerical inaccuracies:

1. Insufficient accurate scf thresholds.
2. Exchange correlation energy is computed in real space. LDA should be preferred as compared to GGA here.
3. Z* calculation requires a very dense k-point sampling which is not accurate enough sometimes.

Acoustic Sum Rules are then imposed to make these inaccuracies to go.

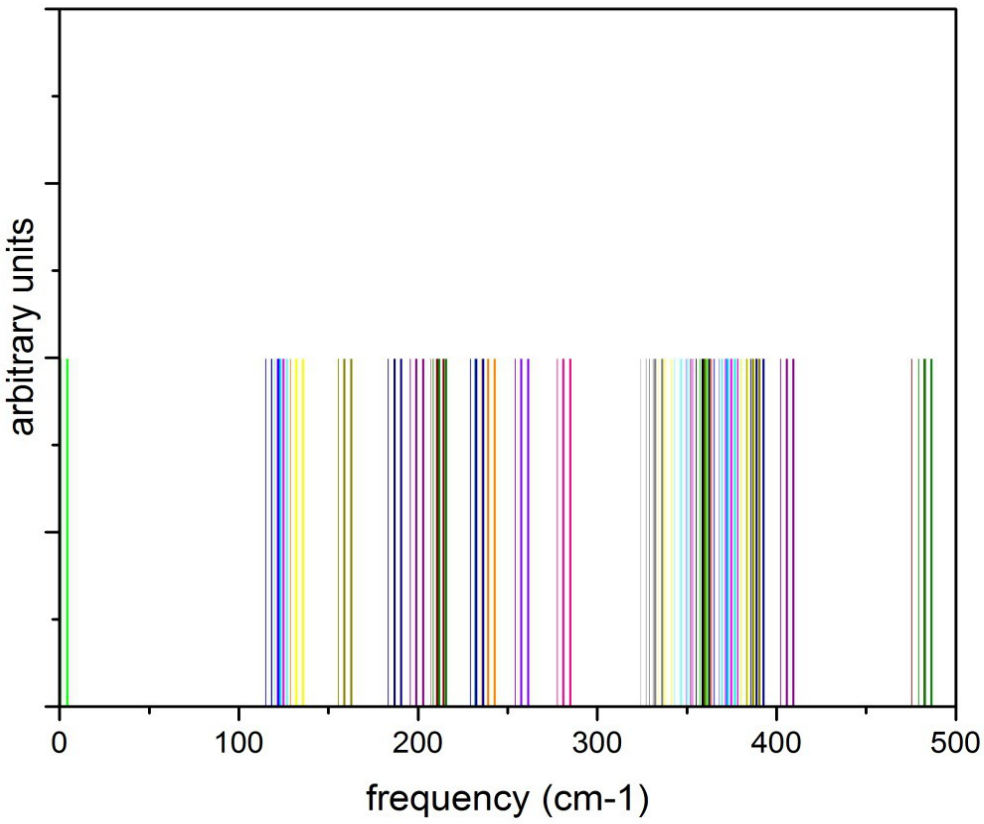


Figure 17: Acoustic and Optical modes in $TiSi_2$

Acoustic modes at the gamma point are zero while the rest 33 are optical modes.

Some of these modes are even Raman active. Now, I'll introduce the concept of Raman Spectroscopy. It is a technique used to observe vibrational, rotational and other frequency modes in a system. When some laser light is impinged on a compound, it interacts with molecular vibrations, phonons or other excitations in the system. This leads to energy of laser photons to shift up or down. And, hence the compound is detected.

In C49 $TiSi_2$ compound, Raman active modes are in the range 250 – 350 cm^{-1}.

CONCLUSIONS

I have used DFT to perform a set of self-consistent calculations to study structural and some bulk properties of C49 $TiSi_2$. I began with performing VC relax calculations to relax the system. The lattice parameters obtained after the calculation were very close to the input theoretical values put in by me. Then, density of states calculations was performed. Maximum number of available states was around the Fermi level. DOS does not become zero around the Fermi level, suggesting that the compound is highly conducting. These calculations were then followed by the projected density of states calculations. It can be seen that d- orbitals of Ti contribute most to the DOS. This is because d- orbitals have empty states which can be filled on excitation of the compound, making it conducting. Following this, bands structure calculations were done which tell about the conducting nature of the compound. There is no band gap in its band structure. Comparisons have been made with Si's and Ti's band structure plot. $TiSi_2$ is even more conducting than Ti metal which can be seen from the dispersion. After this, Charge density calculations leading to charge density plots were done. Charge density contour plots are in 010 planes. The plot tells about the bonding in the crystal. Si atoms have strong directional bonding between each other. Between Ti atoms there is no directional bonding, between Si and Ti atoms there is weak directional bonding. So, it has both covalent and metallic nature. At last, I calculated the phonon modes at the gamma point. In total 36 modes were obtained. First 3 correspond to the acoustical modes and rests are the optical modes. The Raman active modes are in the range 250 – 350 cm^{-1}.

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